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Low Dimensional Correlated Systems: $CuGeO_3$ and NaV_2O_5

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Some of the properties of the low dimensional electronically correlated materials $CuGeO_3$ and NaV_2O_5 are discussed. The emphasis lies on recent results obtained using Raman scattering and optical absorption spectroscopy as a function of temperature, magnetic field and hydrostatic pressure.

Keywords: Correlated systems; Low dimensional: Phase diagrams; Spin-Peierls; Charge ordering; Optical spectroscopy

1 INTRODUCTION

Low dimensional correlated systems show a wide variety of physically interesting and unusual properties. Well known in this field are the copper-oxides showing high temperature superconductivity [1], and the low dimensional spin systems such as the spin-Peierls compound $CuGeO_3$ [2], the Sr-Cu-O ladder compounds [3], the superconducting

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chain/ladder compound $Sr_{14-x}Ca_xCu_{24}O_{41}$ [4], and the recently discovered charge ordering compound NaV_2O_5 [5]. One of the interesting aspects of one dimensional spin chains with isotropic interactions is that the presence of a continuous symmetry prevents spontaneous ordering [6]. In these systems ordering may occur only through coupling to other degrees of freedom, such as lattice or charge excitations. The transition to a singlet ground state in $CuGeO_3$ is, for instance, a direct result of the spin-phonon coupling in this system.

In this contribution, a few of the fascinating properties of low dimensional correlated systems –in particular of $CuGeO_3$ and NaV_2O_5– are briefly discussed. Section 2 introduces the compounds $CuGeO_3$ and NaV_2O_5. Section 3 discusses the nature of spin-excitations and the occurrence of bound states in low dimensional spin systems. Section 4 addresses the $(H-T)$ phase diagram of in particular $CuGeO_3$. Finally section 5 discusses charge ordering in NaV_2O_5, and presents some ideas on low energy charge excitations in this compound.

2 $CuGeO_3$ AND NaV_2O_5

2.1 The spin-Peierls compound $CuGeO_3$

$CuGeO_3$ is the first example of an inorganic compound [2] showing a spin-Peierls transition [7]. Characteristic fingerprints of a spin-Peierls transition are the formation of a singlet ground state, as evidenced by a vanishing magnetic susceptibility; the formation of a superstructure, as evidenced by the appearance of superlattice reflections in diffraction experiments [8, 9]; and the opening of a spin gap in the magnetic excitation spectrum, as evidenced in for instance inelastic neutron scattering experiments [10].

The spin-chains in $CuGeO_3$ are formed by unpaired d-electrons on Cu^{2+} ions which are magnetically linked into chains along the orthorhombic c-direction by an almost 90° Cu-O-Cu super exchange path. The chains are separated from each other by GeO_4 units. The existence of weak inter-chain couplings makes this compound quasi-one dimensional ($J_c \approx 120$ K, $J_b \approx 16$ K, $J_a \approx 2$ K) [10]. In addition, there is a substantial next nearest neighbor interaction ($J_{nn} \approx 160$ K, $J_{nnn} \approx 40$ K) [11, 12]. The transition temperature in $CuGeO_3$ is $T_c \approx 14$ K, and the gap in the magnetic excitation spectrum is found to be 2.1 meV [10, 13].

2.2 The charge ordering compound NaV_2O_5

Initially NaV_2O_5 was thought to be a spin-Peierls compound with $T_c \approx 34$ K [5]. Also in this case an exponentially vanishing susceptibility was observed as well as the formation of a superstructure and the opening of a spin-gap ($\Delta \approx 10$ meV [14]). Moreover, the temperature dependent susceptibility in the high temperature phase shows the typical Bonner-Fisher behaviour [15] expected for an antiferromagnetic $S = 1/2$ spin chain [5]. Recent experimental findings [16, 17, 18] suggest, however, that this compound is not a spin-Peierls compound but rather a charge ordering compound [18-22].

At high temperatures, NaV_2O_5 may be considered as a quarter filled ladder system [23]. The rungs ($\parallel a$) of the ladders ($\parallel b$) are formed by two Vanadium ions (VO_5 pyramids) with intermediate valence 4.5+. The V ions are connected through 180° V-O-V bonds. The $a - b$ ladder layers are separated in the c-direction by Na ions. At high temperatures spin-chains are formed by the rungs, each containing one unpaired electron. At low temperature a charge ordering occurs, where the two V ions on a single rung become inequivalent, *i.e.* they now have different $(4.5 \pm \delta)$ valence states. The ordering occurs most likely in a zig-zag pattern along the ladders.

3 SPIN EXCITATIONS AND BOUND STATES

Spin excitations in antiferromagnetic compounds are classically described by spin-wave theory. In quantum spin systems, however, this simple theory is no longer sufficient. Instead of having a dispersion branch describing well defined spin waves, one now has spinons as elementary excitations. These $S = \frac{1}{2}$ spinons do not occur as single particles, but rather form a two-particle triplet excitation continuum [24]. In addition to that the interaction between these triplets may lead to the formation of bound states and additional continua which may be of singlet, triplet or even quintuplet nature. Such bound states have indeed been observed. In $CuGeO_3$ it reveals itself [25, 26] as a well defined mode at 30 cm^{-1} (see figure 1a)). Its singlet nature is evidenced by the lack of field dependence in the dimerized phase ($H < 12.5$ T). In the high field phase ($H > 12.5$ T) the bound state mode either moves to lower energy or disappears all together.

In NaV_2O_5 the situation is a bit more complex. Also here one finds newly activated modes in the low temperature phase [27, 28, 29]

(see figure 1b). In this case, however, several modes are observed – at 66, 106, and 132 cm^{-1} – that have been interpreted as singlet bound states [27], as low lying Vanadium d-level excitations [29], or as folded phonon excitations which energy and intensity is strongly renormalized due to spin-phonon interactions [30]. Presently, the exact origin of these low energy modes is still under intense debate. The availability of inelastic neutron scattering data, as well as an improved understanding of in particular the low energy dynamics in NaV_2O_5 appear to be a prerequisite for a full understanding of these low energy modes.

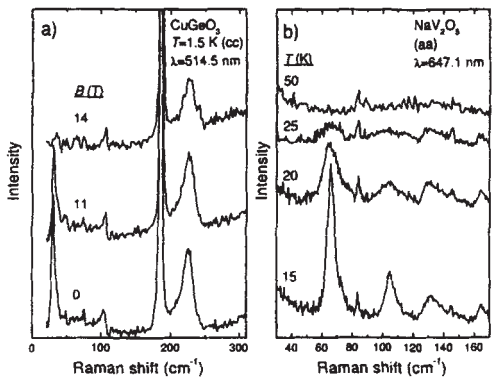

FIGURE 1: a) Polarized (cc) Raman spectra of $CuGeO_3$ at $T = 1.5$ K for H =0, 11, and 14 T [31]. b) Polarized (aa) Raman spectra of NaV_2O_5 for $T = 15$, 20, 25 and 50 K [29]

4 THE $(H - T)$ PHASE DIAGRAM

One of the characteristic properties of a spin-Peierls compound is its $(H - T)$ phase diagram (see figure 2) consisting of a uniform phase $(T > T_c)$, a dimerized phase $(T < T_c;\ H < H_c)$, and a modulated phase for high fields $(T < T_c;\ H > H_c)$. For $CuGeO_3$, this general structure is experimentally well supported (see for instance [32]). The full phase diagram of NaV_2O_5 has not yet been determined. It has been shown, however, that the phase transition is rather insensitive to applied fields [17], strongly supporting the idea that this is not a spin-Peierls, but rather a charge ordering compound.

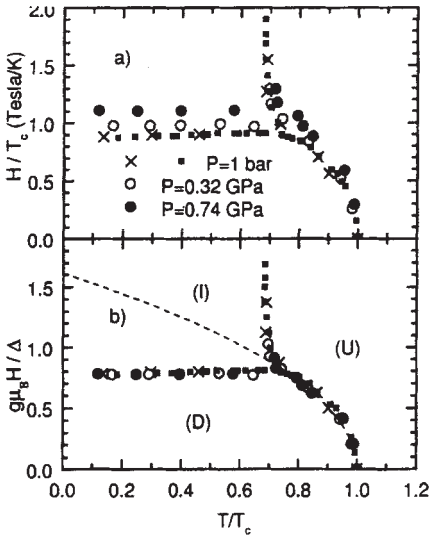

FIGURE 2: Phase diagram of $CuGeO_3$ for different pressures plotted versus T/T_c [33]; a) scaling of H with T_c and b) scaling of H with Δ_{ST}. The solid squares are data obtained at 1 bar by magnetostriction/thermal expansion measurements [32].

Standard theory predicts the phase diagram of a spin-Peierls compound to scale as H/T_c and T/T_c [34]. Optical absorption experiments on $CuGeO_3$, in which T_c was varied by applying hydrostatic pressure, have shown that this this compound does not follow this scaling (figure 2a). Instead a H/Δ, T/T_c type of scaling has been found (figure 2b), where Δ is the spin-gap (about 2.1 meV in $CuGeO_3$ [10]) at zero magnetic field. This observed H/Δ scaling may not be so surprising: the gap state has a triplet character, and therefore shows a linear splitting in a magnetic field. A phase transition is expected when the lowest energy triplet state energetically crosses the ground state. The surprising observation is, however, that the first-order phase transition into the incommensurate phase occurs already when the gap from the ground state to the lowest triplet state is still about $\Delta/4$, *i.e.* at much lower magnetic fields than intuitively expected. These observations call for a theory going beyond the standard Cross-Fisher theory. They also call for a reexamination

of the organic spin-Peierls compounds, where in particular an accurate determination of spin-gap value is of interest. An initial test for H/Δ scaling, based on spin-gaps determined from susceptibility experiments, has indeed already shown that these compounds may show a similar scaling behaviour [33].

5 CHARGE ORDERING AND EXCITATIONS IN NaV_2O_5

The charge ordering transition in NaV_2O_5 occurs at $T = 34$ K. This relatively low transition temperature implies that there should be a low energy scale for the charge dynamics of NaV_2O_5. On first sight, the interactions determining the charge dynamics are the intersite Coulomb interactions, and the intersite hopping terms. These interactions, however, have typical energies of about 0.5 eV. It is not easy to see how these high energies may lead to a low energy scale.

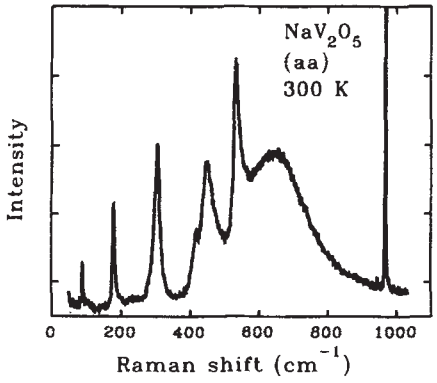

FIGURE 3: Room temperature (aa)-Polarized Raman spectrum of NaV_2O_5 [35].

Experimentally there is some evidence from optical spectra that such a low energy scale indeed exists [29, 36, 37]. Raman scattering, for instance, shows a broad band in the (aa) spectra, already at room temperature (see fig. 3). One of the origins of this scattering continuum might be high energy spin excitations activated through an exchange coupling process, similar as in $CuGeO_3$ [26]. The energy

of the observed band is, however, incompatible with this. From the exchange interaction $J = 560$ K [5] of NaV_2O_5, one would expect two magnon scattering to occur around 1000 cm^{-1} and not around 500 cm^{-1} as observed. Furthermore, one would expect this scattering to occur in a (bb)-polarized configuration (*i.e.* with light polarizations along the dominant exchange direction), whereas the low energy continuum is observed in (aa)-polarization only (*i.e.* polarizations along the rungs).

Presently, the low energy scale is still an open question. There is a simple single ladder model which gives some first insight in this problem [35]. In this model, the only parameters are the Coulomb interaction, V, between vanadium ions on different rungs along the ladder, and the hopping, t, between ions on a single rung. The Hamiltonian for this system is given by

$$H = t \sum_i (c^+_{i,l} c_{i,r} + c^+_{i,r} c_{i,l}) + V \sum_{i,s=l,r} \rho_{i,s} \rho_{i+1,s}, \qquad (1)$$

where $c_{i,s}$ ($c^+_{i,s}$) are electron annihilation (creation) operators for site s on the i^{th} rung, and $\rho_{i,s}$ are the charge densities on these sites. As long as $|V| < t$, this Hamiltonian leads to a homogeneous charge distribution on the rungs, *i.e.* the average position of the electron on the rung is at the center. Starting from this equilibrium state, it clear that the *classical* elementary excitations in such a system are charge waves involving small displacements of the average electron position. The dispersion of these excitations is easily derived from eq. (1) to give $E_k = 2t\sqrt{(1 + (V/t)\cos(k \cdot x))}$, where k is the momentum along the ladder, and x is in the ladder direction. At $k = 0$ these are relatively high energy excitations with uniform charge displacements along the rungs (possibly observable in a polarized infrared spectra [36]). The excitations at $k = \pi/a$ have an alternating charge displacement, and have a low energy provided that $V \sim t$. These may indeed be Raman active, in a (aa)-configuration through a two particle process involving states with momentum $\pm k$.

For $V > t$ the Hamiltonian eq. (1) leads to a zig-zag charge ordered phase with a charge disproportionately $\delta = \sqrt{1 - (t/V)^2}$. The typical low energy excitations would then be charge solitons – which can be envisioned as kinks in the zig-zag pattern – with typical energy $(V - t)^{3/2}$ [38, 39]. Provided that V is of the order of t, this indeed gives again the low energy scale.

The fact that NaV_2O_5 charge orders, implies that $V \sim t$ for the present simple model eq. (1). So within the above model one can easily understand the occurrence of low energy charge waves and charge solitons. The question is, however, how this is stabilized. Any small variation of either V or t would directly lead to drastic changes in the charge dynamics, as well as to the phase transition itself. Another problem is that eq. (1) considers a single chain only. This approach is of course not ideal. The presence of long range Coulomb interactions and inter-ladder hopping terms requires inclusion of neighboring ladders too [18-22] Hopefully more elaborate models can resolve these problems, and give a full understanding of the charge ordering and the low energy charge dynamics in NaV_2O_5.

6 CONCLUSION

Low dimensional, correlated spin and charge systems show a wide variety of intriguing physical phenomena. Many of these phenomena may be understood using one dimensional models, which theory can handle quite well. Many of the interesting phenomena arise due to the interactions between the various degrees of freedom such as the spin-Peierls transition in $CuGeO_3$, and the charge ordering transition and formation of a singlet ground state in NaV_2O_5.

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